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(71) Applicant
Lonseal Corp.
4-15-3 Midori, Sumida-ku, Tokyo

(72) Inventor
Toshio Ohama
c/o Lonseal Corp., Tsuchiura Office, 5-3 Higashi-Nakanuki-cho, Tuchiura City, Ibaraki Prefecture
Takeshi Watanab
c/o Lonseal Corp., Tsuchiura Office, 5-3 Higashi-Nakanuki-cho, Tuchiura City, Ibaraki Prefecture

(54) [Title of the Invention]

Resin Composition Sheet Film Prepared from It

(57) [Abstract]

[Object]

The object is to provide a polyester resin composition, wherein the good transparency as a characteristic of amorphous polyester resin is maintained; the peelability from metal rollers is good; at the same time, there is hardly any plate out on metal rollers; and moreover, no vertical stripes due to catching air while rolling sheets or films are not generated.

[Means to Accomplish the Object]

Polyester resin composition for calender molding comprising 100 parts by weight of amorphous polyester resin, 0.2-3.0 parts by weight of fatty acid having 20 or more carbon atoms and 0.01-3.0 parts by weight of organic phosphate ester with the amount of the organic phosphate set at the same or below the amount of the fatty acid and sheet or film prepared by carrying out calender molding the composition.

[Patent Claims]

[Claim 1]

A polyester resin composition for calender molding characterized by comprising 100 parts by weight of a polyester resin made of a repeating unit consisting a dicarboxylic acid component, 80 mole% or more of which is one kind or a mixture of 2 or more kinds selected from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid and isophthalic acid and glycol component, 80 mole% or more of which is one kind or a mixture of 2 or more kinds selected from ethylene glycol, neo-pentyl glycol, diethylene glycol and 1,4-cyclohexanedimethanol compounded with 0.2-3.0 parts by weight of fatty acid and 0.01-3.0 parts by weight of organic phosphate ester.

[Claim 2]

The polyester resin composition for calender molding of Claim 1. wherein the amount of the organic phosphate ester is same as or less than the amount of the fatty acid.

[Claim 3]

A sheet or film characterized by carrying out calender molding of the polyester resin composition of Claim 1 or 2.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of the Invention]

This invention pertains to a polyester resin composition for calender molding and sheet or film prepared by carrying out calender molding of the resin composition.

[0002]

[Prior Art]

Crystalline polyethylene terephthalate resin (called PET resin, below) comprising a repeating unit of terephthalic acid and ethylene glycol has been used previously as a molding material for the products of various applications, and those sheet or film moldings among the products have been used in a wide range of application fields such as wrapping materials for foods and medicines, covering materials for containers, materials for blister packing containers, lamination for sheets used in building, home appliance and automotive applications, etc.

[0003]

In the case of sheet molding by using a PET resin, the extrusion molding method is conventionally used. The extrusion molding is a molding process carried out by discharging a molten resin through a die adjusted to obtain a specific sheet thickness and taking up the molten sheet while quenching it at a temperature below the softening temperature. In the case, the peeling of the sheet prepared from the takeup rollers was easy, but there were shortcomings such as being liable to form partially uneven thickness even if the die is adjusted accurately yielding poor sheet

thickness accuracy causing troubles in the post-finishing processes such as printing, lamination, coating, etc., and at the same time, holes in the sheet at the time of secondary molding such as vacuum or pressurized molding. In addition, in the case of molding of sheets by using the extrusion molding method, the molding speed is slow, and consequently, the productivity is not necessarily good.

[0004]

Because of the above reasons, the calender molding method is frequently used instead of the extrusion molding method for the production of sheets or films. The calender molding method is a molding process carried out by rolling a molten resin with heated metal rollers (calender rollers) to sheets or films of desired thickness. It does not have troubles occurring the proximity of the die in the case of extrusion molding, the thickness accuracy of sheets or films prepared is excellent providing the products of excellent quality, at the same time, the molding speed is fast giving excellent productivity, and consequently, the method is suitable for manufacturing of products of the same specification.

[0005]

However, it has been practically impossible to prepare sheets or films of crystalline PET resins by using the calender molding method. The reasons why the calender molding is difficult to be used are the melt tensile force of molten crystalline PET resins at a temperature above the melting point being extremely small and calender molding requiring relatively high melt tensile force as well as the melting point of crystalline PET resins being high and limitation in the temperature setting of calender molding machines.

[0006]

Therefore, various research and development studies have been carried out to change the workability and physical properties by changing PET resin chemical structures. Specifically, the crystallinity was controlled by partially substituting terephthalic acid or ethylene glycol of PET with other components to obtain random copolymers, some of which were completely amor-

phous. As a result of such an art of crystallinity control, it became possible to improve physical properties including high transparency, and there was a possibility of using calender molding.

[0007]

However, in the case of highly polar resins such as PET resins, the adhesion to the heated metal rollers (calender rollers) is significant, and as a result, the calender molding of the resin alone is impossible. To solve this problem, the compounding of the resin with various additives has been proposed. Those examples are found in the Japanese Kokai Patent Application Publication Nos. Hei 11[1999]-343,353, 2000-186,191, 2000-302,951, 2000-327,891, 2001-64,496, etc. As an additive for achieving easy peelability from metal rollers, those showing low affinity with the resin have been generally said to be effective. However, if such an additive is compounded, it is often led to reduced transparency of sheets or films molded or plate out on the metal rollers. Consequently, even if the crystallinity of the resin is controlled to modify the properties to be suitable for calender molding, it has been very difficult to carry out any calender molding of PET-type polyester resins without damaging transparency, and at the same time, causing plate out on the metal rollers but with easy peeling from the metal rollers.

[0008]

[Object of the Invention]

This invention has been carried out under the circumstances described above, and its object is to provide a polyester resin composition, wherein the good transparency as a characteristic of PET-type polyester resins, especially crystallinity-controlled polyester resins (amorphous polyester resins) is maintained; the peelability from metal rollers is good; at the same time, there is hardly any plate out on metal rollers; and moreover, no vertical stripes due to catching air while rolling sheets or films are not generated and sheet or film obtainable by carrying out calender molding of the polyester resin composition.

[0009]

[Means to Accomplish the Object]

The inventors of this invention studied diligently to accomplish the above object, as a result, they found that the object described above was accomplishable by using a resin composition of a specific polyester resin compounded with specified amounts of specific additives as a polyester resin composition for calender molding and arrived at this invention.

[0010]

Specifically, the polyester resin composition of this invention is characterized by comprising 100 parts by weight of a polyester resin made of a repeating unit consisting a dicarboxylic acid component, 80 mole% or more of which is one kind or a mixture of 2 or more kinds selected from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid and isophthalic acid and glycol component, 80 mole% or more of which is one kind or a mixture of 2 or more kinds selected from ethylene glycol, neo-pentyl glycol, diethylene glycol and 1,4-cyclohexanedimethanol compounded with 0.2-3.0 parts by weight of fatty acid and 0.01-3.0 parts by weight of organic phosphate ester. In this case, the amount of the organic phosphate ester is preferably same as or below the amount of the fatty acid compounded. Furthermore, the sheet or film of this invention is characterized by being prepared by carrying out calender molding of the polyester resin composition of this invention described above.

[0011]

[Preferred Embodiment of the Invention]

The preferred embodiment of this invention is explained in detail as follows. The polyester resin of this invention is made of a repeating unit consisting a dicarboxylic acid component, 80 mole% or more of which is one kind or a mixture of 2 or more kinds selected from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid and isophthalic acid and glycol component, 80 mole% or more of which is one kind or a mixture of 2 or more kinds selected from ethylene glycol, neo-pentyl glycol, diethylene glycol and 1,4-cyclohexanedimethanol.

[0012]

Moreover, among those various possible examples, it is preferable to use a polyester resin having a repeating unit of a dicarboxylic acid component, 90 mole% or more of which is terephthalic acid and glycol component comprising 10-95 mole% of 1,4-cyclohexanedimethanol and 90-5 mole% of ethylene glycol, and in addition, the specific polyester resin used is suitably amorphous. If the polyester resin used is amorphous, it is possible to obtain a molten form at a relatively low temperature, thus it is advantageous for calender molding requiring large melt tensile force, and at the same time, the transparency and surface smoothness of sheets or films prepared after calender molding are good. The non-crystallinity of polyester resins is variable depending on the monomer component composition, and to obtain a good workability of calender molding as well as amorphous property, the resin comprises preferably 100% of terephthalic acid with 30-90 mole% of ethylene glycol and 70-10 mole% of 1,4-cyclohexanedimethanol. Furthermore, the repeating unit of the resin is optimally made of 100% of terephthalic acid with 65-80 mole% of ethylene glycol and 35-20 mole% of 1,4-cyclohexanedimethanol.

[0013]

A polyester resin preferable usable in this invention can be prepared by carrying out he reaction of a dicarboxylic acid component mostly containing terephthalic acid and glycol component containing ethylene glycol and 1,4-cyclohexanedimethanol and subsequent polycondensation in the presence of a specific catalyst. Specifically, a colorless and transparent copolyester can be prepared by carrying out the reaction of a dicarboxylic acid component containing at least 90 mole% of terephthalic acid with a glycol component comprising 10-95 mole% of 1,4-cyclohexanedimethanol and 90-5 mole% of ethylene glycol at a temperature sufficient to carry out esterification or transesterification and subsequently polycondensation of the reaction product under absolute pressure below 1.333 Kpa for a period of time shorter than 2 hr in the presence of a catalyst comprising 0-75 ppm of Mn, 50-150 ppm of Zn, 5-20 ppm of Ti, 5-200 ppm of Ge and 10-80 ppm of P based on the weight of the copolyester to be prepared and inhibitor system.

[0014]

Furthermore, 80 mole% or more of the dicarboxylic component of the polyester resin of this invention comprises one kind or a mixture of two or more kinds of dicarboxylic acids selected from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid and isophthalic acid. The remaining 20 mole% may comprises succinic acid, glutaric acid, adipic acid, sebacic acid, suberic acid, azelaic acid, dodecanedioic acid, fumaric acid, maleic acid, itaconic acid, ortho-phthalic acid, 2,6-naphthalenedicarboxylic acid, 2,6-naphthalenedimethylene-carboxylic acid, para-phenylenedicarboxylic acid, etc. Moreover, the dicarboxylic acid component of 20 mole% or less may contain a small amount of trivalent or tetravalent carboxylic acids so that the molecular structure of the polyester resin may have long-chain branching introduced. As a result of this long-chain branching introduction to the polyester resin molecular structure, the melt tension can be improved, and it becomes suitable for calender molding. Incidentally, as a trivalent carboxylic acid, there are trimellitic acid, etc., and as a tetravalent carboxylic acid, there are pyromellitic acid, etc.

[0015]

On the other hand, as a glycol component usable in the polyester resin of this invention, there are ethylene glycol, neo-pentyl glycol, diethylene glycol and 1,4-cyclohexanedimethanol used alone or as a mixture of two or more kinds to occupy 80 mole% or more of the total glycol component compounds. As a glycol for the remaining 20 mole% of the glycol component, there are, for example, propylene glycol, 1,3-propanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2,2-dimethyl1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isopropyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, thiodiethanol, 1,2-cyclohexane-dimethanol, 1,3-cyclohexanedimethanol, , 2,2,4,4-tetramethyl-1,3-cyclobutanediol, etc. Moreover, the 20 mole% or less of the glycol component may also contain a small amount of trihydric or tetrahydric alcohols to introduce long-chain branching in the molecular structure of the polyester resin. As a trihydric alcohol, there are trimethylolpropane, etc., and as a tetrahydric alcohol, there are pentaerythritol, etc.

[0016]

The molecular weight of the polyester resin of this invention is not especially limited, but if the numerical average molecular weight is less than 10,000, the melt tension of the molten resin is so small that the moldable temperature range in the case of calender molding is narrowed, and on the other hand, if the numerical average molecular weight is over 200,000, the viscosity of the molten resin becomes so large that the load to the calender molding facility becomes too high, or the surface smoothness of sheets or films prepared becomes inferior. Therefore, considering the load to the calender molding facility, securing a wide range of molding conditions and good surface smoothness of sheets or films to be prepared, the numerical average molecular weight of the polyester resin of this invention is preferably in the range of 10,000-200,000.

[0017]

The molecular weight distribution of the polyester resin of this invention is also not especially restricted. However, to achieve sufficiently large melt tension required for calender molding and low viscosity for the purpose of reducing the load to the molding facility simultaneously, it is effective to allow the overall molecular weight distribution to be wide or add a slight amount of a super-high molecular weight resin as conventionally carried out. It is possible to achieve this during the polymerization reaction, but the method mixing the same kind of polyester resins having different molecular weight levels is generally convenient.

[0018]

Incidentally, as a specific example of the polyester resin of this invention, there are also commercially available products. For example, amorphous polyester resins comprising 100 mole% of terephthalic acid, 60-75 mole% of ethylene glycol and 40-25 mole% of 1,4-cyclohexanedimethanol are available from Eastman Chemical Products, Inc., with trade names of Kodar PETG Copolyester grade Eastar PETG 6763, Tsunami Copolyester grade GS1, GS2, GS3, GS4, etc., and these products are suitably used in this invention.

[0019]

On the other hand, the fatty acid compounded with the polyester resin in this invention is limited to a fatty acid having 20 or more carbon atoms. Specifically, the smaller the number of carbon atoms in the fatty acids, the more the evaporation at a low temperature. Consequently, if a fatty acid with less than 20 carbon atoms is compounded, the amount of evaporation is too large at a temperature in the range of 170-220°C suitable for calender molding of polyester resins to maintain good peeling from the metal rollers or prevent a problem of variable peelability from the metal rollers depending on the conditions used from occurring. Therefore, to achieve easy peelability from the metal rollers of calender molding of polyester resins at a suitable temperature range, the fatty acid is required to be one having 20 or more carbon atoms.

[0020]

As a fatty acid having 20 or more carbon atoms, there are behenic acid, tetracosanoic acid, hexacosaqnoic acid, peptacosanoic acid, montanic acid, triacontanoic acid, dotriacontanoic acid, etc. Highly pure products of these fatty acids are commercially available as reagents, but in many cases, they are expensive and generally not used as additives to resin compositions. However, some of those fatty acids having 20 or more carbon atoms, particularly montanic acid, etc., are available at low prices, and in this invention, those fatty acids for addition to resins including montanic acid are preferably used.

[0021]

When the polyester resin is compounded with a fatty acid having 20 or more carbon atoms, the glass transition temperature of the polyester resin is characteristically reduced. This indicates that the polyester resin and fatty acid having 20 or more carbon atoms are liable to be miscible. In general, as an additive to add to resins to improve their peelability from metals, those additives having low affinity and being difficult to be mixed with the resins, but those fatty acids having 20 or more carbon atoms are easily mixed with polyester resins and at the same time, the peelability of these polyester resins from metals is characteristically improved. Consequently, the characteristics of this invention having excellent transparency of sheets or films molded and no plate out occurrence as well as good peelability from the metal rollers are considered to be

achieved. This aspect of those fatty acids having 20 or more carbon atoms is a point different from other mold-releasing agents and lubricants for polyester resins.

[0022]

The amount of such a fatty acid having 20 or more carbon atoms to be compounded with the polyester resin of this invention is in the range of 0.2-3.0 parts by weight per 100 parts by weight of the polyester resin. If the content of the fatty acid having 20 or more carbon atoms is less than 0.2 part by weight, the peelability from the metal rollers becomes insufficient, but on the other hand, if it is over 3.0 parts by weight, the transparency of sheets or films prepared is reduced. Therefore, to achieve stable easy-peelability from the metal rollers and high transparency of sheets and films prepared in the calender molding of this invention, the amount of the fatty acid having 20 or more carbon atoms is restricted in the range of 0.2-3.0 parts by weight per 100 parts by weight of the polyester resin.

[0023]

In addition to the fatty acid having 20 or more carbon atoms in the polyester resin composition of this invention, it is essential to add an organic phosphate ester. If the fatty acid having 20 or more carbon atoms is used, and its amount to be compounded is specified, it is possible to prepare a sheet or film easily peelable from the metal rollers and having good transparency, but in the case of calender molding, the fused resin accumulated between the metal rollers (generally called bank) is liable to pick up air bubbles, which may appear as vertical stripes on the surface of sheets or films prepared. To prevent this problem, the use of an organic phosphate ester concomitantly used with the fatty acid having 20 or more carbon atoms is effective.

[0024]

The organic phosphate ester in this case is an organic phosphate ester and partially saponified organic phosphate ester, and one kind or mixture of 2 or more kinds is usable. The organic phosphate ester in this case is not especially restricted, specific examples include esters of monostearyl phosphate, distearyl phosphate, tristearyl phosphate, dilauryl phosphate, trilauryl phosphate, monononylphenylpolyoxyethylene phosphate, dinonylphenylpolyoxyethylene phos-

phate, trinonylphenylpolyoxyethylene phosphate, monolaurylpolyoxyethylene phosphate, dilaurylpolyoxyethylene phosphate, trilaurylpolyoxyethylene phosphate, monodecylpolyoxyethylene phosphate, didecylpolyoxyethylene phosphate, tridecylpolyoxyethylene phosphate, monododecylpolyoxyethylene phosphate, didodecylpolyoxyethylene phosphate, tridodecylpolyoxyethylene phosphate, monooctylpolyoxyethylene phosphate, dioctylpolyoxyethylene phosphate, trioctylpolyoxyethylene phosphate, monododecylpolyoxyethylene phosphate, didodecylpolyoxyethylene phosphate, tridodecylpolyoxyethylene phosphate, monostearyldilauryl phosphate, monolauryldistearyl phosphate, monostearyldinonylphenylpolyoxyethylene phosphate, monononylphenylpolyoxyethylenedistearyl phosphate, monolauryldinonylphenylpolyoxyethylene phosphate, mononononylphenylpolyoxyethylenedilauryl phosphate, monostearyldilaurylpolyoxyethylenedistearyl phosphate, monolaurylpolyoxyethylenedistearyl phosphate, monolauryldilaurylpolyoxyethylene phosphate, monolaurylpolyoxyethylenedilauryl phosphate, etc., and these phosphates can be used alone or as a mixture of 2 or more kinds. There are commercially available products of some of those organic phosphate esters as a resin additive, and the use of those products is preferable from the economic standpoint.

[0025]

The kind of the partially saponified product of organic phosphate ester of this invention is not especially restricted. There are saponified products of the above mono- or di-phosphates with the remaining acid base portion. Namely, there are calcium-, magnesium or zinc-saponified products of the above organic phosphate esters. Specific examples are calcium-saponified product of monostearyl phosphate, magnesium-saponified product of monostearyl phosphate, zinc-saponified product of monostearyl phosphate, calcium-saponified product of monolauryl phosphate, magnesium-saponified product of monolauryl phosphate, zinc-saponified product of monolauryl phosphate, calcium-saponified product of mononononylphenylpolyoxyethylene phosphate, magnesium-saponified product of mononononylphenylpolyoxyethylene phosphate, zinc-saponified product of mononononylphenylpolyoxyethylene phosphate, calcium-saponified product of monolaurylpolyoxyethylene phosphate, magnesium-saponified product of monolaurylpolyoxyethylene phosphate, zinc-saponified product of monolaurylpolyoxyethylene phosphate, etc., and these compounds may be used alone or as a mixture of 2 or more kinds. There are commer-

cially available products of some of those partially saponified products of organic phosphate esters as a resin additive, and the use of those products is preferable from the economic standpoint.

[0026]

The amount of an organic phosphate ester compounded with the polyester resin of this invention is in the range of 0.01-3 parts by weight per 100 parts by weight of the polyester resins. Even if the amount of this organic phosphate ester added is small, the problem when the fatty acid alone is used can be solved, but if the amount compounded is less than 0.01 part by weight, the desired effect is not satisfactorily exhibited, an don the other hand, if the amount compounded is over 3.0 parts by weight, the transparency of sheets prepared is reduced. Therefore, to maintain high transparency of polyester resins as well as exhibiting the effect organic phosphate ester, the amount of the organic phosphate ester to be compounded is desirably in the range of 0.01-3.o parts by weight.

[0027]

Furthermore, if the amount of the organic phosphate ester compounded is higher than that of the fatty acid, the peelability from the metal rollers becomes slightly inferior, and under certain conditions, it becomes difficult to carry out calender molding. Therefore, to carry out calender molding stably under a wide range of molding conditions and prepare a sheet or film with a good appearance, the amount of the organic phosphate ester to be compounded is same or below the amount of the fatty acid compounded.

[0028]

For the purpose of improving the peelability of the polyester composition of this invention with the above fatty acid and organic phosphate ester compounded from the metal rollers further, the concomitant use of fatty acid ester- or oxidized polyethylene wax may be effective in some cases. The effects of the fatty acid ester- or oxidized polyethylene wax improving the peelability is large, and consequently, it is liable to cause transparency reduction of plate out. Therefore, if it is to be compounded, the amount used is required to be held at a small amount. Specifi-

cally, the amount is below the amount of the fatty acid or organic phosphate ester, and at the same time, it is preferably below 0.5 parts by weight.

[0029]

In the fatty acid ester type was usable in this case, the number o carbon atoms in the fatt acid portion is not especially limited. However, considering the volatility of the ester obtained, the use of synthetic or natural wax of esters of aliphatic saturated carboxylic acids having 12-28 carbon atoms and aliphatic saturated alcohols having 2-30 carbon atoms is preferable. As an aliphatic saturated fatty acid having 2-30 carbon atoms for synthetic wax, there are lauric acid, myristic acid, stearic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, etc. As an aliphatic saturated alcohol having 2-30 carbon atoms, there are, for example, monohydric alcohols such as ethyl alcohol, octyl alcohol, lauryl alcohol, stearyl alcohol, behenyl alcohol, pentacosyl alcohol, ceryl alcohol, octacosyl alcohol, melisyl alcohol, etc.; dihydric alcohols such as ethylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, etc., and polyhydric alcohols, for example, trihydric alcohols such as glycerol, etc.

[0030]

As a specific example of the synthetic wax, there are, for example, stearyl laurate, stearyl myristate, stearyl stearate, octyl behenate, lauryl behenate, myristic behenate, stearyl behenate, behenyl behenate, pentacosyl behenate, ceryl lignocerate, octacosyl lignocerate, melisyl lignocerate, stearyl cerotate, behenyl cerotate, ceryl cerotate, melisyl cerotate, ethyl montanate, ceryl montanate, glycol montanate, etc. Furthermore, as a natural wax, there are, for example, montan wax, carnauba wax, bees wax, candelilla wax, bran wax, privet wax, etc. Considering volatility and peelability from the metal rollers, the use of glycol montanate, montanate glyceride or montan wax is preferable. These substances are commercially available as a resin additive, and it is economical to sue these products..

[0031]

The kind of the oxidized polyethylene is not especially limited, and low- or high-density wax is usable. Considering the peelability from the metal rollers, partially oxidized polyethylene

wax having an acid number of 1-40 mgKOH/g and weight average molecular weight below 10,000 is preferably used. These substances are also commercially available as a resin additive, and it is economical to use those products.

[0032]

The polyester resin composition of this invention for calender molding can be prepared by simply mixing a polyester resin in its pellet or power form, fatty acid having 20 or more carbon atoms, organic phosphate ester, an dif necessary, fatty acid ester or oxidized polyethylene wax or melting and kneading in a kneading machine. Any of known kneaders is usable in this case, but because of the ease of handling and ability for uniform dispersion, the use of single or double axial extruder, kneader, co-kneader, planetary mixer, Banbury mixer, etc., is preferable.

[0033]

Furthermore, the polyester resin composition of this invention for calender molding can be prepared by obtaining a high-concentration mixture (generally called master batch) of polyester resin, fatty acid, organic phosphate ester and fatty acid ester or oxidized polyethylene wax, in advance, and subsequently, simply mixing with the polyester resin or melting and kneading the master bath with the polyester resin. The above master batch may be prepared suitably by also using a kneader selected from those examples shown above.

[0034]

On the other hand, the polyester resin composition of this invention may be compounded with various additives within the range of not damaging the workability in the calender molding. Specific examples of such additives include previously known hindered phenol, thioether, amine or phosphate type antioxidants; benzophenone, benzoate, benzotriazole, cyanoacrylate and hindered amine type UV absorbents; anionic, cationic or nonionic low molecular weight or polymeric antistatic agents; thickening agents such as epoxy compounds, isocyanate compounds, etc.; coloring agents such as dyes, pigments, etc.; UV blockers such as titanium oxide, carbon black, etc.; reinforcing materials such as glass fiber, carbonfiber, etc.; fillers such as silical clay, calcium

carbonate, barium sulfate, glass beads, talc, etc.; flame retardants; plasticizers; foaming agents; anti-microbial agents; anti-fungal agent; fluorescent dyes; surfactants; cross-linking agents; etc.

[0035]

Moreover, the polyester resin composition of this invention may have thermoplastic resins such as polyolefins, polyvinyl chloride, polystyrenes, polyethers, polyesters, polyamides, polyimides, etc., within the range not damaging the workability in the calender molding.

[0036]

, the polyester resin composition of this invention is a resin composition suitable for the preparation of sheets or films by carrying out melt kneading in a mixer, single or double-axial kneader and molding by using a calender molding machine. At the time of the preparation of sheets or films, the peelability of the molten resin from the metal rollers is good, and the transparency of sheets or films prepared is excellent. In addition, no plate out on the metal rollers is generated, and no vertical stripes due to catching air while rolling sheets or films are generated. Therefore, it is possible to prepare sheets or films of excellent appearance in high productivity by carrying out calender molding of the polyester resin of this invention.

[0037]

The sheets or films prepared by carrying out calender molding of the polyester resin composition of this invention are suitably usable as transparent or colored sheets or films on decorative boards, sheets or films for cards, sheets or films for various wrapping materials, etc.

[0038]

[Application Example]

This invention is explained further in detail by specifically using application examples, but this invention is not necessarily limited to these application examples.

[0039]

<Application Example 1>

The polyester resin used was Kodar PETG Copolyester grade Eastar PETG 6763 manufactured by Eastman Chemical Products Inc. (called [A1], below). The polyester resin [A1] had 100 mole% of terephthalic acid as a dicarboxylic acid component and no other dicarboxylic acid. Furthermore, its glycol component comprised 60-75 mole% of ethylene glycol and 40-25 mole% of 1,4-cyclohexanedimethanol, and no other glycol was used. It was a polyester resin in a pellet form made of a repeating unit comprising those dicarboxylic acid and glycol components, and the numerical average molecular weight was 26,000. The polyester resin [A1] showed no responses corresponding to melting of crystal or crystallization of molten form in the measurements carried out by using a differential scanning calorimeter, and thus, it was amorphous. As a fatty acid having 20 or more carbon atoms, montan wax [Licoeax S manufactured by Clariand Japan (K.K.), called [B1], below]. The organic phosphate ester used was a 6:4 by weight mixture of monostearyl phosphate ester and distearyl phosphate ester [FAX-518 manufactured by Daikyo Kasei Kogyo (K.K.), called [C1], below]. The polyester resin [A1], fatty acid [B1] and organic phosphate ester [C1] were mixed in the weight ratio of [A1]:[B1]:[C1]=100:0.75:0.75, 0.5 part by weight of phenol=type antioxidant (Adekastab AO-60 manufactured by Asashi Denka Kogyo K.K., called AO-60, below) was added, and the composition was molded to a sheet by using conventional calender molding procedures. Specifically, the polyester [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] were mixed homogeneously in a Henshel mixer, the mixture was kneaded in a Banbury mixer till the resin temperature reaches a temperature in the range of 160-175°C to obtain a polyester resin composition. The composition prepared was rolled in a reversed L-shaped calender molding machine with 4 rollers maintained at a constant temperature, and after completing takeup and cooling stages, a sheet of 150 μm thick and 1,000 mm wide was prepared. In the sheet molding process, the peelability of the material (molten resin) from the calender rollers, any presence of plate out on the calender rollers and any presence of vertical stripes due to catching air were evaluated, and at the same time, as an index of the transparency of sheets, the following sample and method were used to measure haze. Furthermore, the results of respective evaluation items were judged based on the following evaluation standards. Table 1 shows the results of evaluation obtained in the respective applica-

tion examples, and Table 2 shows the results of evaluation in the respective comparative examples.

[0040]

[Haze measurement]

The method of JIS K 7105 was used for haze measurements carried out by using a Suga Shikenki (K.K.) direct-reading haze computer (Model HGM-2D). From the center portion of a 150 μm thick sheet prepared by calender molding, 5 plates of 5x5 cm were cut out for measurement, and the mean of those results was used.

[0041]

[Evaluation standards]

(1) Evaluation of peelability from metal rollers

Peelability evaluation 1: prior to carrying out calender molding, a simple measurement of peelability from metal was evaluated by using a small mixer. The small mixer used was a Toyo Seiki Seisakusho (K.K.) 60 cc laboratory mixer (Model R-60). The temperature of the mixer was set at 180°C, the kneading was carried out at 60 rpm for 10 min, and subsequently, the peelability of the molten mixture from the mixer was evaluated. This evaluation was carried out prior to calender molding, and if the result of the evaluation showed no peelability, no subsequent calender molding was carried out because of insufficient peelability. If the result of peelability evaluation carried out by using a small mixer was found to be good, the calender molding was carried out, and the peelability was evaluated as follows.

Peelability evaluation 2: if it was possible to peel of the molten resin in a sheet form from the calender rollers, it was considered good (O), and if it was adhered on the rollers, it was considered bad (X).

(2) Evaluation of plate out on metal rollers

If no plate out was generated on the calender rollers set at 190°C while carrying out molding continuously for 2 hr, the result was considered good (O), and if the plate out was observed, the result was considered bad (X).

(3) Evaluation of vertical stripe formation due to catching air whole rolling

If the sheet prepared has no vertical stripes because of no air-catching in the rolling stage with the calender rollers, the result was considered good (O), and if the sheet had vertical stripes formed, the result was considered bad (X).

(4) Transparency evaluation

If the result of haze measured was less than 5%, the result was considered excellent (⊕), if the haze was 5% or over but below 10%, the result was considered good (O), and if the haze was 10% or over, the results was considered bad (X). If the result was excellent (⊕) or good (O), the sheet transparency was considered good.

[0042]

<Application Example 2>

A polyester resin composition comprising the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 1 was used, but the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:1.05:0.06, and the same other procedures as those in the application example 1 were used.

[0043]

<Application Example 3>

A polyester resin composition comprising the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 1 was used, but the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or

more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:0.75:1.5, and the same other procedures as those in the application example 1 were used.

[0044]

<Application Example 4>

The polyester resin [A1], as a fatty acid having 20 or more carbon atoms, behenic acid (manufactured by Kosei K.K. as an additive, called [B2], below) and organic phosphate ester [C1] were respectively used, the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B2] and organic phosphate ester [C1] was set at [A1]:[B2]:[C1]= 100:1.05:0.06, and the same other procedures as those in the application example 1 were used.

[0045]

<Application Example 5>

The polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and as an organic phosphate ester, zinc-saponified product of monostearyl phosphate ester (EL-508A manufactured by Eishinn Kasei K.K., called [C2], below) were respectively used, the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C2] was set at [A1]:[B1]:[C2]= 100:1.05:0.06, and the same other procedures as those in the application example 1 were used.

[0046]

<Application Example 6>

The polyester resin used was Tsunami Copolyester grade GS2 manufactured by Eastman Chemical Products Inc. (called [A2], below). The polyester resin [A2] had 100 mole% of terephthalic acid as a dicarboxylic acid component and no other dicarboxylic acid. Furthermore, its glycol component comprised 60-75 mole% of ethylene glycol and 40-25 mole% of 1,4-cyclohexanedimethanol, and no other glycol was used. It was a polyester resin in a pellet form made of a repeating unit comprising those dicarboxylic acid and glycol components, and the numerical average molecular weight was 25,000. The polyester resin [A2] showed no responses

corresponding to melting of crystal or crystallization of molten form in the measurements carried out by using a differential scanning calorimeter, and thus, it was amorphous. The composition ratio by weight of the polyester resin [A2], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A2]:[B1]:[C1]= 100:1.05:0.06, and the same other procedures as those in the application example 1 were used.

[0047]

<Application Example 7>

A polyester resin composition comprising the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 1 was used. However, a master batch with he fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] compounded in high proportion was prepared in advance, and the master batch prepared was compounded with a constant amount of the polyester resin [A1] to obtain a composition of a desired mixing ratio. The master batch was prepared so that the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:7.5:0.4, and for its preparation, a double axial extruder with a cylinder diameter of 35 mm was used. The master batch prepared was mixed with a constant amount of the polyester resin so that the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:1.05:0.06, 0.5 part by weight of the antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide.

[0048]

<Application Example 8>

A polyester resin composition comprising the polyester resin [A2], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 6 was used. However, a master batch with he fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] compounded in high proportion was prepared in advance, and the master batch prepared was compounded with a constant amount of the polyester resin [A2] to

obtain a composition of a desired mixing ratio. The master batch was prepared so that the composition ratio by weight of the polyester resin [A2], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A2]:[B1]:[C1]= 100:7.5:0.4, and for its preparation, a double axial extruder with a cylinder diameter of 35 mm was used. The master batch prepared was mixed with a constant amount of the polyester resin [A2] so that [A2]:[B1]:[C1]= 100:1.05:0.06, 0.5 part by weight of the antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide.

[0049]

<Application Example 9>

A polyester resin composition comprising the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 1 was compounded with a fatty acid ester. As a fatty acid ester, the ester of montanic acid and 1,4-butanediol (Clariant Japan K.K., montanic acid wax Licowax E, called [D1], below) was used. The composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1], organic phosphate ester [C1] and fatty acid ester [D1] was set at [A1]:[B1]:[C1]:[D1]= 100:0.75:0.04:0.04, 0.5 part by weight of the antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide.

[0050]

<Application Example 10>

A polyester resin composition comprising the polyester resin [A2], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 6 was compounded with an oxidized polyethylene wax. As an oxidized polyethylene wax, a product with an acid number of 15-19 mgKOH/g (Clariant Japan K.K., Licowax PED191, called [D2], below) was used. The composition ratio by weight of the polyester resin [A2], fatty acid having 20 or more carbon atoms [B1], organic phosphate ester [C1] and oxidized polyethylene wax [D2] was set at [A2]:[B1]:[C1]: [D2]= 100:0.75:0.04:0.04, 0.5 part by weight of the antioxi-

dant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide.

[0051]

<Comparative Example 1>

The polyester resin used was the polyester resin [A1], and 100 parts by weigh of the polyester resin [A1] was compounded with 0.5 part of phenol-type antioxidant (AO-60). The peeling test to use a small mixer was carried out for the polyester resin composition prepared, but the peeling was impossible because of the molten resin was strongly adhered to the mixer. The calender molding was carried out because it was considered impossible to prepare a sheet of this polyester resin composition comprising the polyester resin [A1] and antioxidant by using a calender molding machine.

[0052]

<Comparative Example 2>

The same peeling test with a small mixer as that of the comparative example 1 was carried out except the polyester resin used was the polyester resin [A2]. No calender molding was carried out because the peeling of the molten resin from the mixer was impossible.

[0053]

<Comparative Example 3>

The polyester resin composition used was a polyester resin composition comprising the polyester resin [A1] and fatty acid having 20 or more carbon atoms [B1], and no organic phosphate ester was compounded. The mixing ratio of the polyester resin [A1] and fatty acid having 20 or more carbon atoms [B1] was set at [A1]:[B1]=100:1.05 by weight, 0.5 part of an antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide. The sheet prepared showed vertical stripes due to air catching while rolling. The result of this comparative example indicate, the formation of vertical stripes due to air catching while rolling cannot be inhibited if

the polyester resin composition comprises the polyester resin [A1] and fatty acid having 20 or more carbon atoms [B1] alone.

[0054]

<Comparative Example 4>

The polyester resin composition used was a polyester resin composition comprising the polyester resin [A1] and organic phosphate ester [C1] with stearic acid (Kanto Kagaku K.K., powder reagent of 95% purity, called [B3], below) as a fatty acid having less than 20 carbon atoms compounded. The mixing ratio of the polyester resin [A1], fatty acid having less than 20 carbon atoms [B3] and organic phosphate ester [C1] was set at [A1]:[B3]:[C1]=100:3.0:0.06 by weight, 0.5 part of an antioxidant (AO-60) was added, and the same peeling test with a small mixer as that used in the comparative example 1 was carried out. As a result, the peeling of the molten resin from the mixer was impossible, and no calender molding was carried out.

[0055]

<Comparative Example 5>

The polyester resin composition used was a polyester resin composition comprising the polyester resin [A1] and organic phosphate ester [C1], and no fatty acid was compounded. The mixing ratio of the polyester resin [A1] and organic phosphate ester [C1] was set at [A1]:[C1]=100:1.5 by weight, 0.5 part of an antioxidant (AO-60) was added, and the same peeling test with a small mixer as that in the comparative example 1 was carried out. As a result, the peeling of the molten resin from the mixer was found insufficient, and no calender molding was carried out.

[0056]

<Comparative Example 6>

A polyester resin composition comprising the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 1 was used, but the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]=

100:0.15:0.04. Subsequently, 0.5 part of an antioxidant (AO-60) was added, and the same peeling test with a small mixer as that in the comparative example 1 was carried out. As a result, the peeling of the molten resin from the mixer was found insufficient because of partial adhesion of the molten resin to the mixer, and no calender molding was carried out.

[0057]

<Comparative Example 7>

A polyester resin composition comprising the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] similar to the application example 1 was used, but the composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:3.5:0.06. Subsequently, 0.5 part of an antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide. The results of this comparative example imply that the transparency is reduced if the amount of the fatty acid having 20 or more carbon atoms [B1] compounded is too large.

[0058]

<Comparative Example 8>

The composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:1.05:0.005. Subsequently, 0.5 part of an antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide. The results of this comparative example imply that if the amount of the organic phosphate ester [C1] compounded is too low, the effect inhibiting the formation of vertical stripes on the sheet surface is not exhibited.

[0059]

<Comparative Example 9>

The same procedures as those in the comparative example 8 were carried out except that the organic phosphate ester [C1] was substituted with the partially saponified product of organic phosphate ester [C2]. The results obtained in this comparative example imply that the effect inhibiting the formation of vertical stripes on the sheet surface is not exhibited if the amount compounded is too low even though the organic phosphate ester was substituted with a partially saponified product of the organic phosphate ester.

[0060]

<Comparative Example 10>

The composition ratio by weight of the polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and organic phosphate ester [C1] was set at [A1]:[B1]:[C1]= 100:1.05:3.5. Subsequently, 0.5 part of an antioxidant (AO-60) was added, and the same subsequent procedures as those in the application example 1 were carried out to obtain a sheet of 150 μm thick and 1,000 mm wide. The results of this comparative example imply that if the amount of the organic phosphate ester [C1] compounded is too high, the peelability from the calender rollers becomes insufficient, especially, if the roller temperature is set high to make the sheet surface smooth, the peelability becomes poor, and at the same time, the transparency is also reduced.

[0061]

<Comparative Example 11>

The same procedures as those in the comparative example 10 were carried out except that the organic phosphate ester [C1] was substituted with the partially saponified product of organic phosphate ester [C2]. The results obtained in this comparative example imply that the peelability from the calender rollers becomes poor if the amount compounded is too high even though the organic phosphate ester was substituted with a partially saponified product of the organic phosphate ester. Especially, if the roller temperature is set high to make the sheet surface smooth, the peelability becomes poor, and at the same time, the transparency is also reduced.

[0062]

<Comparative Example 12>

The polyester resin [A1], fatty acid ester [D1] used in the application example 9 instead of fatty acid and organic phosphate ester [C1] were respectively used. The composition ratio by weight of the polyester resin [A1], fatty acid ester [D1] and organic phosphate ester [C1] was set at [A1]:[D1]:[C1]= 100:1.05:0.06, and the same subsequent procedures as those in the application example 1 were carried out. The results obtained in this comparative example imply that the peelability from the calender rollers is achievable by using the fatty acid ester [D1] instead of the fatty acid [B1], but it causes plate out.

[0063]

<Comparative Example 13>

The polyester resin [A2], oxidized polyethylene wax [D2] used in the application example 10 instead of the fatty acid and organic phosphate ester [C1] were respectively used. The composition ratio by weight of the polyester resin [A2], oxidized polyethylene wax [D2] and organic phosphate ester [C1] was set at [A2]:[D2]:[C1]= 100:1.05:0.06, and the same subsequent procedures as those in the application example 1 were carried out. The results obtained in this comparative example imply that the peelability from the calender rollers is achievable by using the oxidized polyethylene wax [D2] instead of the fatty acid having 20 or more carbon atoms [B1], but it causes plate out.

[0064]

<Comparative Example 14>

The polyester resin [A1], polyethylene wax (Clariant Japan K.K., Licowax PE520, called [D3], below) instead of the fatty acid and organic phosphate ester [C1] were respectively used. The composition ratio by weight of the polyester resin [A1], polyethylene was [D3] and organic phosphate ester [C1] was set at [A1]:[D3]:[C1]= 100:3.0:0.06, and after adding 0.5 part by weight of an antioxidant (AO-60), the same peeling test in a small mixer as that of the comparative example 1 was carried out. As a result, the peeling of the molten resin from the mixer was impossible, and no calender molding was carried out.

[0065]

<Comparative Example 15>

The polyester resin [A2], ethylene bisstearicamide (Clariant Japan K.K., Licolub FA1, called [D4], below) instead of the fatty acid and organic phosphate ester [C1] were respectively used. The composition ratio by weight of the polyester resin [A2], ethylene bisstearicamide [D4] and organic phosphate ester [C1] was set at [A2]:[D4]:[C1]= 100:3.0:0.06, and after adding 0.5 part by weight of an antioxidant (AO-60), the same peeling test in a small mixer as that of the comparative example 1 was carried out. As a result, the peeling of the molten resin from the mixer was impossible, and no calender molding was carried out.

[0066]

<Comparative Example 16>

The polyester resin [A2], acrylic acid polymer lubricant (Mitsubishi Rayon, metablend L-1000, called [D5], below) instead of the fatty acid and organic phosphate ester [C1] were respectively used. The composition ratio by weight of the polyester resin [A2], polymer lubricant [D5] and organic phosphate ester [C1] was set at [A2]:[D5]:[C1]= 100:3.0:0.06, and after adding 0.5 part by weight of an antioxidant (AO-60), the same peeling test in a small mixer as that of the comparative example 1 was carried out. As a result, the peeling of the molten resin from the mixer was impossible, and no calender molding was carried out.

[0067]

<Comparative Example 17>

The polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and fatty acid ester [D1] used in the application example 9 were respectively used, and the same procedures as that of the application example 2 except the organic phosphate ester [C1] was substituted with the fatty acid ester [D1]. The results obtained in this comparative example imply that the effect inhibiting vertical stripe formation due to air catching while rolling is not exhibited, if the fatty acid ester [D1] is used instead of the organic phosphate ester [C1].

[0068]

<Comparative Example 18>

The polyester resin [A1], fatty acid having 20 or more carbon atoms [B1] and oxidized polyethylene wax [D2] used in the application example 10 instead of organic phosphate ester were respectively used, and the same procedures as that of the application example 2 except the organic phosphate ester [C1] was substituted with the oxidized polyethylene wax [D2]. The results obtained in this comparative example imply that the effect inhibiting vertical stripe formation due to air catching while rolling is not exhibited, if the oxidized polyethylene wax [D2] is used instead of the organic phosphate ester [C1].

[0069]

[Table 1]

Application example	Composition	Mixing ratio (part)	Peeling	Plate out	Stripes	Transparency
1	[A1]/[B1]/[C1]	100/0.75/0.75	O	O	O	⊕
2	[A1]/[B1]/[C1]	100/1.05/0.06	O	O	O	⊕
3	[A1]/[B1]/[C1]	100/0.78/1.5	O	O	O	O
4	[A1]/[B2]/[C1]	100/1.05/0.06	O	O	O	⊕
5	[A1]/[B1]/[C2]	100/1.05/0.06	O	O	O	⊕
6	[A2]/[B1]/[C1]	100/1.05/0.06	O	O	O	⊕
7	[A1]/[B1]/[C1]	100/1.05/0.06	O	O	O	⊕
8	[A2]/[B1]/[C1]	100/1.05/0.06	O	O	O	⊕
9	[A1]/[B1]/[C1]/[D1]	100/0.75/0.04/0.04	O	O	O	⊕
10	[A2]/[B1]/[C1]/[D2]	100/0.75/0.04/0.04	O	O	O	⊕

[0070]

[Table 2]

Comaprative example	Composition	Mixing ratio (part)	Peeling	Plate out	Stripes	Transparency
1	[A1]	100	X			
2	[A2]	100	X			
3	[A1]/[B1]	100/1.06	O	O	X	⊕
4	[A1]/[B3]/[C1]	100/3.0/0.06	X			
5	[A1]/[C1]	100/1.5	X			
6	[A1]/[B1]/[C1]	100/0.15/0.04	X			
7	[A1]/[B1]/[C1]	100/3.5/0.06	O	O	O	X
8	[A1]/[B1]/[C1]	100/1.05/0.005	O	O	X	⊕
9	[A1]/[B1]/[C2]	100/1.05/0.005	X	O	O	X
10	[A1]/[B1]/[C1]	100/1.05/3.5	O	X	O	X
11	[A1]/[B1]/[C2]	100/1.05/3.5	O	X	O	X
12	[A1]/[D1]/[C1]	100/1.05/0.06	O	X	O	O

13	[A2]/[D2]/[C1]	100/1.05/0.06	O	X	O	O
14	[A1]/[D3]/[C1]	100/3.0/0.06	X			
15	[A2]/[D4]/[C1]	100/3.0/0.06	X			
16	[A2]/[D5]/[C1]	100/3.0/0.06	X			
17	[A1]/[B1]/[D1]	100/1.05/0.06	O	O	X	O
18	[A1]/[B1]/[D2]	100/1.05/0.06	O	O	X	O

* The blank spaces in the table have no results because of the peelability evaluated in the peeling test to sue a small mixer, and no calender molding was carried out.

[0071]

[Effect of the Invention]

As apparent from the results of evaluation shown in Table 1 and Table 2, the polyester resin composition of this invention shows hardly any adhesion to the metal rollers (calender rollers) of calender molding for crystallinity-controlled polyester resins (amorphous polyester resins) and plate out on the metal rollers, at the same time, the transparency of sheets or films prepared is excellent, th sheets or films have no vertical stripes due to air catching at the time of rolling, and the composition is suitable for the high speed production of sheets or films by calender molding.